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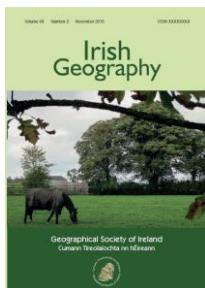
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Stable oxygen isotopes in Irish oaks: potential for reconstructing local and regional climate

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Abstract: The long Irish oak tree-ring chronology, developed for archaeological dating and radiocarbon calibration, is the longest of any in northwest maritime Europe, spanning most of the Holocene (7,272 years). Unfortunately, the rings' widths do not carry a strong climate signal and the record has yet to be satisfactorily applied for dendroclimatic reconstruction. This pilot study explores the potential for extracting a climate signal from Irish oaks by comparing the stable oxygen isotope ratios from ten oak tree cores (*Quercus robur* and *Quercus petraea* L.) collected across the Armagh region of NE Ireland with local and regional climatic and stable isotopic data. Statistically significant correlations between isotope ratios and the amount of summer precipitation ($r = -0.44$) point to the isotopic composition of summer rainfall as the dominant signal. Including the Armagh data into an extended regional oxygen isotope series did not reduce the correlation coefficient with regional precipitation ($r = -0.68$, $p < 0.01$). Correlations of this magnitude in dendro-hydroclimatology are typically restricted to trees growing at their ecological limits. This research suggests that there is considerable potential for including living trees and ancient timbers from Ireland into a regional composite to reconstruct the summer hydroclimate of Britain and Ireland.

Keywords: Tree-rings, *Quercus*, oxygen isotope, Ireland, dendroclimatology.

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Introduction

High resolution climate reconstructions have the potential to extend beyond instrumental records, establishing baseline levels of natural variability, quantifying the frequency of extreme climatic events and allowing evaluation of models used for projections of future climate change (Loader *et al.*, 2003; McCarroll *et al.*, 2015; Luterbacher *et al.*, 2016). Most reconstructions rely heavily on tree-rings and focus on physical properties such as: ring-width (Kelly *et al.*, 2002; García-Suárez *et al.*, 2009), latewood maximum density (Briffa *et al.*, 1988; McCarroll *et al.*, 2013), blue-intensity (McCarroll *et al.*, 2002; Campbell *et al.*, 2011; Björklund *et al.*, 2013) and vessel area (Tardif and Conciatori, 2006; Campelo *et al.*, 2010; Matison and Brümeliš, 2012). More recently, chemical proxies have been exploited, such as the stable isotope ratios of carbon, oxygen and hydrogen (Saurer *et al.*, 1995; Rinne *et al.*, 2010; Seftigen *et al.*, 2011; Young *et al.*, 2012, 2015).

For long-lived tree species, continuous time series can be constructed over hundreds or even thousands of years (Hantemirov and Shiyatov, 2002; Cook *et al.*, 2006; Bale *et al.*, 2011). However, when using shorter-lived species, long chronologies are constructed through the synchronisation of living, archaeological and sub-fossil samples (Loader *et al.*, 2008) to build a composite chronology, extending back beyond the lifespan of any individual tree (Kelly *et al.*, 1989; Briffa *et al.*, 1999; Gagen *et al.*, 2011). The most common species used to construct long chronologies in European temperate regions, belong to the *Quercus* (oak) genus, in particular *Quercus robur* (pedunculate oak), *Quercus petraea* (sessile oak) and their hybrids. Oaks are long-lived trees and the ring-porous structure means that rings are generally clear and unambiguous, so false or missing rings are rare (Baillie, 1973) allowing successful cross-dating (Hilasvuori and Berninger, 2010). Although such long chronologies have been extremely valuable for archaeological dating (Baillie, 1990) and for calibrating the radiocarbon timescale (Friedrich *et al.*, 2004), oak ring-widths are not strongly correlated with climate. Hence, they have been largely rejected for use in palaeoclimate reconstruction (García-Suárez *et al.*, 2009; Young *et al.*, 2012). This is unfortunate, since the Irish oak tree-ring chronology is the longest in NW maritime Europe, extending back 7,272 years (Kelly *et al.*, 2002; Pilcher *et al.*, 1984). Successful characterisation of a robust climate record from this archive could potentially extend annually-resolved climate reconstructions for Ireland over much of the Holocene where at present there are few annually-resolved records and facilitate linkage between the terrestrial, lacustrine and speleothem archives (McDermott *et al.*, 2011, Turner *et al.*, 2015, Swindles *et al.*, 2010, Roland *et al.*, 2015).

In contrast to measures of tree growth, stable isotope ratios within the tree-rings of oaks growing in a temperate climate have been shown to produce strong correlations with climate parameters (Hilasvuori and Berninger, 2010; Labuhn *et al.*, 2013). Hence, this chemical archive provides the potential for extracting palaeoclimate data from localities or species that show weak correlations between climate and physical tree-ring properties such as ring-width. Carbon and oxygen

isotope ratios extracted from cellulose have been employed successfully to reconstruct climate parameters such as temperature, sunshine and precipitation for temperate regions in Europe (Loader *et al.*, 2008; Young *et al.*, 2012, 2015; Rinne *et al.*, 2013). The $\delta^{18}\text{O}$ value of cellulose is controlled by the $\delta^{18}\text{O}$ of precipitation, which is a product of atmospheric circulation, and evaporative enrichment at the leaf surface. Fractionation does not occur when water is taken up by the roots; instead, the critical site for fractionation is within the leaf (Wershaw *et al.*, 1966). Relative humidity and temperature affect transpiration and can cause a difference in vapour pressure between the air and leaf resulting in an evaporative enrichment of $\delta^{18}\text{O}$ at the leaf surface, by as much as 20‰ (Saurer *et al.*, 1998; Roden *et al.*, 2000). Photosynthetic sugars reflect the isotopic signature of leaf water, although they are enriched in ^{18}O by 27‰ in comparison (Labuhn *et al.*, 2013). During the formation of tree-rings, cellulose is formed from sugars which are transported down the trunk where they exchange between 20 and 50% of their oxygen with the source water being carried through the xylem (Barbour and Farquhar, 2000; Labuhn *et al.*, 2013). Therefore, the dominant climatic signal preserved in the $\delta^{18}\text{O}$ of cellulose is a combination of the $\delta^{18}\text{O}$ of precipitation and relative humidity, which is controlled by air mass characteristics and trajectories (Dansgaard, 1964, Treydte *et al.*, 2014, Young *et al.*, 2015, McCarroll and Loader, 2004).

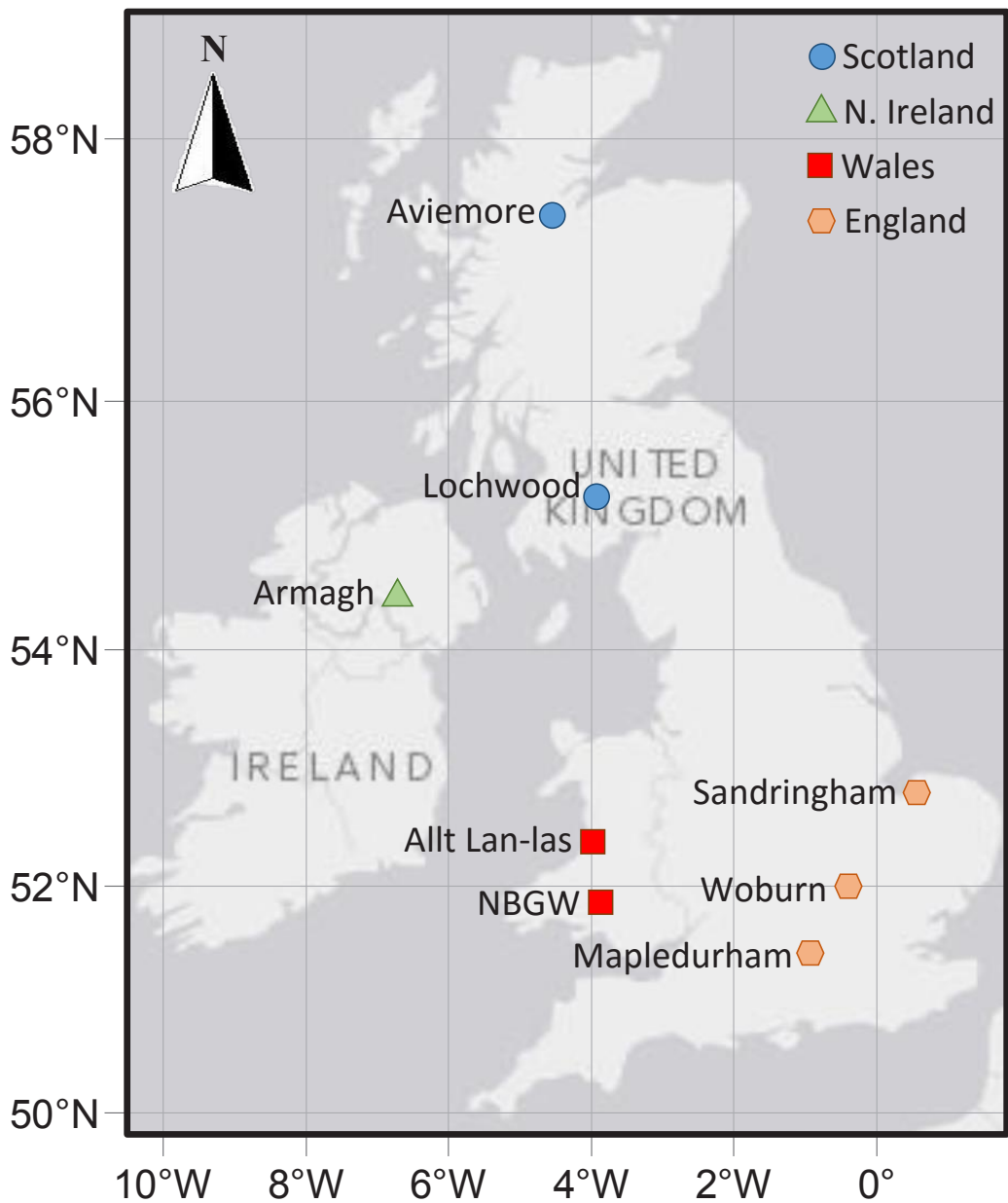
The aims of this study are:

1. To determine whether stable oxygen isotope ratios in Irish oaks carry a climate signal.
2. To determine if the stable isotope ratios from Ireland can be combined with British records to form a composite isotope series for reconstructing climate.

Study site and methodology

Samples of oak were selected from within a 10km radius of the Armagh Observatory (García-Suárez *et al.*, 2009) approximately 700m north-east of the small city of Armagh. The region has a typical temperate, maritime climate (Butler and Coughlin, 1998). Mean annual maximum and minimum temperatures are 12.8°C and 5.6°C respectively, with mean annual precipitation at 816mm and an average annual relative humidity of 85% for the period of AD 1844-2001.

Figure 1: The locations of the Armagh Observatory in Northern Ireland and of the eight $\delta^{18}\text{O}$ chronologies used to form the UK composite.



In order to determine if it is reasonable to include Irish results in a wider reconstruction, the Armagh $\delta^{18}\text{O}$ series was combined with previously published data sets from around the United Kingdom (UK) to form a composite chorology. The seven annually resolved isotope series are well replicated over the common period AD 1880-2001; Lochwood ($55^{\circ}16'\text{N}$ $3^{\circ}26'\text{W}$) (Loader *et al.*, 2008); Sandringham ($52^{\circ}50'\text{N}$ $0^{\circ}30'\text{E}$) (Robertson *et al.*, 2001); Woburn ($51^{\circ}59'\text{N}$ $0^{\circ}35'\text{E}$) (Rinne *et al.*, 2013) and Aviemore ($57^{\circ}19'\text{N}$ $3^{\circ}92'\text{W}$), Allt Lan-las ($52^{\circ}38'\text{N}$ $3^{\circ}92'\text{W}$) and Mapledurham ($51^{\circ}49'\text{N}$ $1^{\circ}26'\text{W}$) (Young *et al.*, 2015). Climate data were obtained from the Armagh Observatory meteorological station ($54^{\circ} 21.2'\text{N}$ $6^{\circ}38.8'\text{W}$) the archives of which contain measurements since AD 1784, and represents the longest continuous meteorological records in Ireland, and one of the longest in the UK (Butler, 1990; Butler and Coughlin, 1998). The UK $\delta^{18}\text{O}$ composite series was calibrated and verified with the 'England and Wales precipitation (EWP) record' (Wigley *et al.*, 1984).

Wood cores of 4mm diameter were obtained using a standard increment borer, and prepared by García-Suárez *et al.*, (2009) using standard dendrochronological methods as described by Stokes and Smiley (1968). The cores were cross-dated against each other using TSAP (RINTEC, Germany) and of the 14 cores provided, 10 were selected for isotopic analysis based upon their consistent inter-tree cross dating ($t \geq 3.5$) (Baillie and Pilcher, 1973), tree-age and ring-clarity. Using a razor blade and microscope, the latewood portion of each annual ring was then removed as thin slivers. Ring porous trees like oak use reserves to build earlywood, so the latewood was targeted to provide true annual resolution (Switsur *et al.*, 1995, Kimak and Leuenberger, 2015, McCarroll *et al.*, in review). The samples were then pooled prior to chemical treatment.

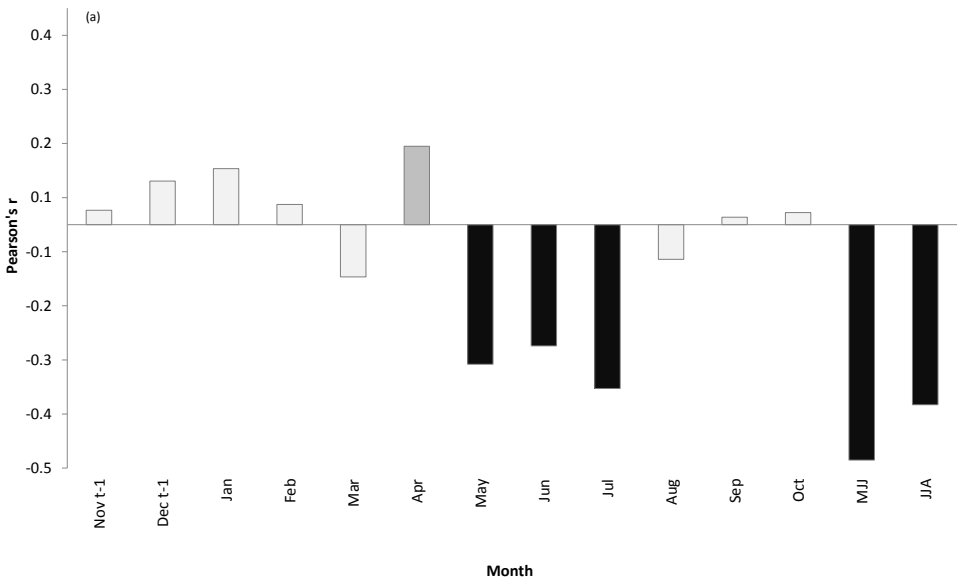
Alpha-cellulose (α -cellulose) was isolated from the pooled latewood samples using standard methods (Loader *et al.*, 1997) and homogenised and freeze-dried (Laumer *et al.*, 2009; Loader *et al.*, 2013). For oxygen isotope analysis, 0.30 to 0.35mg of α -cellulose was weighed into silver foil capsules and then pyrolysed over glassy carbon at 'high temperature' (1400°C) using a Flash HT elemental analyser, interfaced with a Thermo Delta-V isotope ratio mass spectrometer (Thermo Fisher Scientific Inc.) with typical analytical error of $<0.3\text{‰}$ for oxygen. The stable isotope ratios were expressed using delta notations (δ) as per mille (‰) relative to the Vienna Standard Mean Ocean Water (VSMOW) (Coplen, 1995).

Results

Correlations (Pearson's r -values) were calculated between the $\delta^{18}\text{O}$ chronology and mean monthly meteorological parameters obtained from the Armagh observatory for the period AD 1880-2001. The highest values were obtained with precipitation summed over May to July (MJJ) ($r = -0.44$, $p < 0.01$). Weaker correlations were found with July temperature ($r = 0.40$), relative humidity ($r = -0.24$) and sunshine hours ($r = 0.30$) and with the average MJJ temperature ($r = 0.30$), relative humidity ($r = -0.21$) and sunshine ($r = 0.25$). However, step-wise multiple regression, using

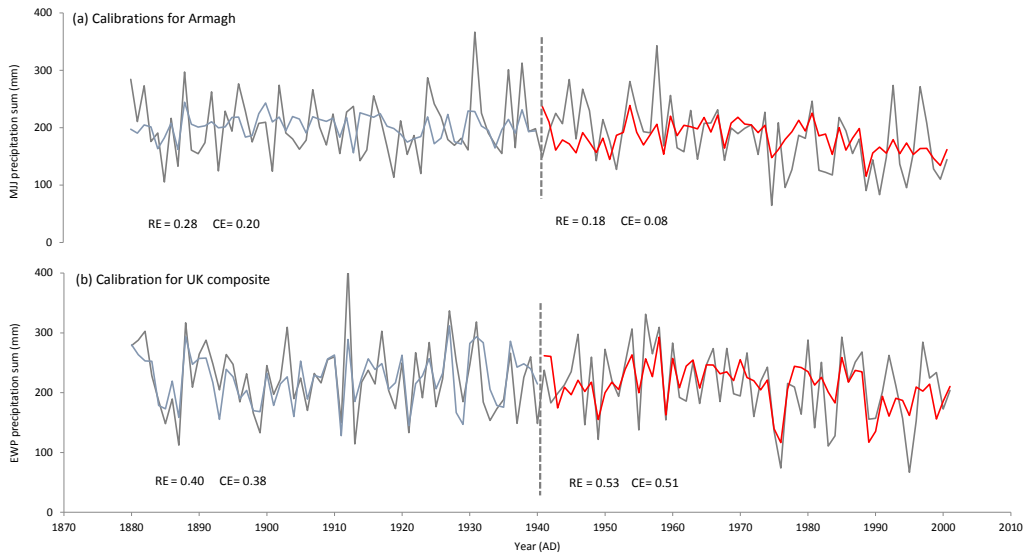
a Bayes' information criterion, discarded these, leaving precipitation as the only climate parameter explaining variance in the Armagh $\delta^{18}\text{O}$ time series ($p < 0.001$).

Figure 2: (a) Composite correlation diagram showing simple linear correlation (Pearson's r) between Armagh $\delta^{18}\text{O}$ and the annual variability of the instrumental data obtained from Armagh Observatory for precipitation. Grey shaded bars represent correlations that are statistically significant with a 95% confidence level and black shaded bars represent correlations with a 99% confidence level. (b) The relationship between Armagh $\delta^{18}\text{O}$ and MJJ precipitation.



Split period calibration and verification, using $\delta^{18}\text{O}$ to reconstruct MJJ precipitation, produced positive values for both Reduction of Error ($\text{RE} = 0.18$ and 0.28) and Coefficient of Efficiency ($\text{CE} = 0.08$ and 0.19). When linear regression is applied over the full period (1880-2001), 19% of the variance is explained (Figure 2b). Thus, the correlation between the Armagh $\delta^{18}\text{O}$ record and local rainfall amount is strongly statistically significant ($p < 0.01$), and as high as some other correlations that have been used for climate reconstruction (McCarroll *et al.*, 2015). However, it falls below the threshold recommended for producing climate reconstructions using variance scaling (McCarroll *et al.*, 2015), so a local reconstruction would have to rely on regression methods, with the loss of variance that ensues.

Figure 3: (a) Calibrations for the Armagh $\delta^{18}\text{O}$ time series; first half calibration period (1941-2001) (red), second half calibration period (1880-1940) (blue), with the sum of MJJ precipitation (mm) from Armagh Observatory (grey); **(b)** Calibrations for the UK $\delta^{18}\text{O}$ composite time series, first half calibration period (1941-2001) (red), second half calibration period (1880-1940) (blue) with the sum of EWP precipitation (mm) from Armagh Observatory (grey).



An alternative to producing a local reconstruction is to include Oxygen isotope data from Ireland into a large regional composite. The individual sites $\delta^{18}\text{O}$ series and the $\delta^{18}\text{O}$ composites were correlated against the Armagh MJJ precipitation sum and the precipitation sum for June to August (JJA) for the England Wales Precipitation series (EWP), which acts a true representation of summer precipitation across southern Central England and Wales (Table 1). There was no statistically significant difference between the correlation coefficients for the Armagh $\delta^{18}\text{O}$ series and both local and regional precipitation ($p > 0.01$).

Table 1: Simple linear correlations (Pearson's r) between $\delta^{18}\text{O}$ series and the Armagh MJJ precipitation record and JJA EWP at various sites across the UK and composite of those sites. (NBGW = National Botanic Gardens Wales).

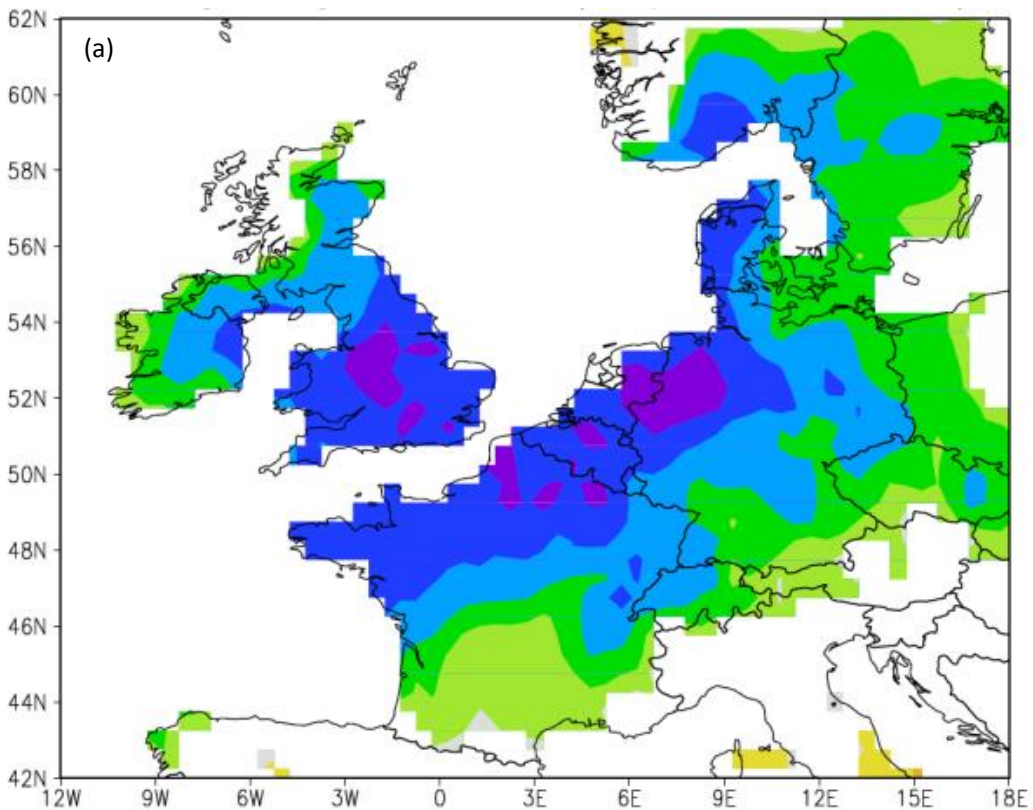
	Armagh MJJ	JJA EWP
Armagh	-0.44	-0.37
UK composite	-0.45	-0.68
Aviemore	-0.15	-0.33
Lochwood	-0.23	-0.47
Allt-Lanlas	-0.44	-0.56
NBGW	-0.13	-0.39
Sandringham	-0.30	-0.53
Woburn	-0.29	-0.50
Oxford	-0.40	-0.50

The individual time series from across the UK were z-scored, and were then averaged to produce $\delta^{18}\text{O}$ composites and then z-scored again. In order to determine the impact of including Armagh, two $\delta^{18}\text{O}$ composites were formed over the common period of 1880-2001. The first covered the UK but excluded the Armagh record, and the second included Armagh. When correlated against JJA EWP both $\delta^{18}\text{O}$ composite series produced the same values, ($r = -0.68$, $p < 0.01$). The skill of the $\delta^{18}\text{O}$ regional composite series (including Armagh) as a proxy for summer precipitation was tested using split period calibration and verification. During the calibration period, 39% of the variance in summer precipitation is explained by the $\delta^{18}\text{O}$ series, and both RE and CE statistics are positive (0.53 and 0.51) (Figure 3b). Over the verification period 53% of the variance is explained with positive RE and CE values (0.40 and 0.38). This demonstrates that a regional $\delta^{18}\text{O}$ composite provides a strong and temporally stable proxy for summer precipitation. Once linear regression was applied over the full series, 46% of the variance was explained.

One of the negative effects associated with using regression-based techniques to reconstruct climate is that it produces a bias towards the mean, and, therefore, underestimates variability and the magnitude of extremes (McCarroll *et al.*, 2015). To avoid this problem, variance scaling (Esper *et al.*, 2005) was used to adjust the $\delta^{18}\text{O}$ composite series to have the same mean and variance as the EWP series. Given the strong correlation, the loss of skill due to scaling (McCarroll *et al.*, 2015) is only 10%. The ability of the scaled reconstruction to capture extreme events was tested using a simple non-parametric test for 'Extreme Value Capture' (McCarroll *et al.*, 2015). Using a 10% threshold to define extreme years, it was found that the UK $\delta^{18}\text{O}$ composite series produced six years above and below the threshold that matched the extreme years in the EWP series which is highly significant ($p < 0.001$) and symmetrical; wet and dry extreme years being captured with equal skill.

Spatial field correlations produced using the new composite $\delta^{18}\text{O}$ time series show large areas of strong correlation. Correlation with summer precipitation is strongly negative (between $r = -0.5$ and $r = -0.6$) for the whole of England and Wales as well as parts of Ireland and the northern regions of France and Germany. Correlations with air pressure at 850mb ($r = 0.5$) now extend across the majority of Britain and Ireland.

Figure 4: Spatial field correlations of the UK composite $\delta^{18}\text{O}$ time series (including Armagh) and gridded JJA climate data using (a) the CRU TS3.22 (land) 0.5° precipitation for AD 1901–2001, and (b) 850mb air pressure during the period AD 1870–2001, produced using 20th century Reanalysis V2 data provided by PSD, Colorado, USA. Coloured bars represent correlation based on Pearson's r ($p < 0.01$). Maps were produced using Climate Explorer (<http://climexp.knmi.nl/>) (Trouet and van Oldenborgh et al., 2013).



Discussion and conclusions

Young *et al.*, (2015) have argued that the dominant control on the stable oxygen isotope ratios of UK oak trees is the oxygen isotopic composition of summer rainfall. Strong correlations between oxygen isotope results occur because dry summers are dominated by cyclonic conditions that produce high isotope ratios in precipitation, whereas wet summers are dominated by anticyclonic conditions (Lamb, 1972) and lower ratios in precipitation. Evaporative enrichment at the leaf level accentuates rather than attenuates the signal. Thus, the dominant control on the isotope ratios is the circulation pattern during the summer. The results from Armagh support these conclusions and since the dominant summer circulation patterns affect large regions it is reasonable to include isotope results from Ireland with those from Great Britain to produce a large scale regional composite series. The results suggest that even with a sparse combination of sub-optimal sites, spread over a relatively large geographic region, there is still a strong relationship between the composite $\delta^{18}\text{O}$ series and both regional summer precipitation amount and summer air pressure.

The Armagh $\delta^{18}\text{O}$ reconstruction for precipitation sum was developed from cores sampled and prepared initially for conventional dendrochronology (García-Suárez *et al.*, 2009). The variance explained was comparable to several other individual sites across the UK. For example, Loader *et al.*, (2008) found a correlation ($r = -0.52$) between cellulose $\delta^{18}\text{O}$ of oak trees and July precipitation at Lochwood, Scotland which was not significantly different to that obtained from Armagh ($p = 0.28$, $P > 0.1$). In contrast, the correlation coefficient from Armagh was significantly different to that found by Rinne *et al.*, (2013) between cellulose $\delta^{18}\text{O}$ and precipitation for southern England ($r = -0.71$). Without knowing specific details about the locations of the samples for this study, it is hard to speculate as to why correlations between $\delta^{18}\text{O}$ and precipitation from Armagh may be lower than other sites in the UK. One possible explanation may relate to the relatively low slope on which the trees were situated (less than 10°), meaning there is the potential for trees to access deep groundwater. This could cause changes in $\delta^{18}\text{O}$ associated with climate to be masked or distorted by sampling 'old' precipitation that is not a true representation of the source water. Other factors including sampling and archival methods, replication, atmospheric pollution, woodland management and ecological amplitude (Fritts, 1976) could also help to explain the relatively lower correlation observed in these trees. Total summer precipitation is not a direct control on the oxygen isotopic composition of cellulose, rather $\delta^{18}\text{O}$ reflects a larger range of external physiological and climatic controls; hence a stronger precipitation signal may be expressed at some sites more than others, such as those where the amount of rainfall does correlate well with the $\delta^{18}\text{O}$ of precipitation. This is likely to occur where soil moisture levels are relatively low, but not low enough to induce moisture stress. Precipitation reconstructions are generally weaker and more variable than those of temperature, possibly due to the localised variations in precipitation and soil moisture levels (Briffa *et al.*, 2002; García-Suárez *et al.*, 2009). Ideally, trees would be selected from sites known to

favour strong isotopic signals such as those located on steep slopes. However, an inherent part of reconstructing climate beyond the period of instrumental data means relinquishing a level of control over sample selection. Thus, this study provides a more realistic representation of potential palaeoclimate reconstructions produced using archaeological and sub-fossil trees in the long Irish oak chronology. By combining multiple sites over a wide region the non-climatic ‘noise’ is averaged out, producing a stronger correlation with the climate data target. The inclusion of Armagh in a UK composite made no difference to the correlation with summer rainfall ($r = -0.68$, $p < 0.01$), with such high results typically being restricted to trees growing at their ecological limits (Loader *et al.*, 2008). This suggests that there is considerable potential for including trees from Northern Ireland into a large regional composite to reconstruct summer precipitation and past changes in circulation. Such a composite might include living trees, building timbers and sub-fossil oaks.

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